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The Painful Derivation of the Refractive Index from Microscopical Considerations

Bernhard J. Hoenders

Abstract The derivation of the refractive index from the microscopical structure of matter is analysed in detail. In particular the many various assumptions leading to the basic Clausius- Mosotti (Lorentz-Lorenz) equation are carefully stated. The most general formulation of the second order correlation theory for the refractive index, the so-called Yvon-Kirkwood theory, is given. These considerations will facilitate the explanation of a very peculiar effect observed by Amat.

Keywords: Refractive index, ATP solution, polarisation, Clausius-Mosotti equation, Lorentz-Lorenz law, effective field.

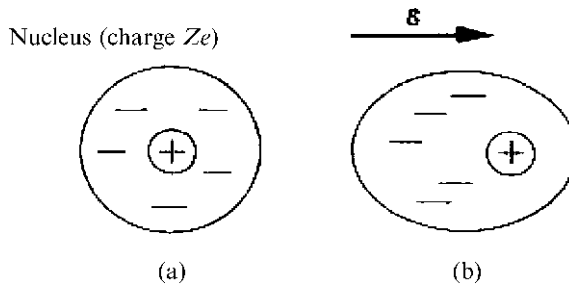
Introduction

When measuring the refractive index of an ATP solution in water Amat observed that the refractive index of this solution was increasing during the illumination and even kept on increasing when the illumination was stopped! A similar effects, though less pronounced was observed in a solutions of ADP. A solution of AMP did not show the effect. References to his work are [1, 2, 3]. An explanation of this effect is still lacking. Because the refractive index is the key quantity which is measured, the key thoughts leading to the concept “refractive index” have to be clearly stated in order to get an understanding of the Amat effect. This contribution to the conference provides all the essential thoughts which, starting from the basic microscopical quantity, viz. the microscopical polarisability, leads to the macroscopical concept “refractive index”. The polarisation of a medium originates from the effect of an electric field on a electrically neutral atom or molecule: The electric field displaces the negatively charged electron cloud from the positively charged nucleus, thus inducing a net electric field as the field of the positive- and negative

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charges no longer compensate each other outside the atom. The resulting field is the dipole field far away from the atom. Near the atom corections must be added known as the quadripole- octipole- etc. fields.



(a) The unpolarised atom, (b) The polarised atom

In the macroscopic theory of the electrodynamics of continuous media, the electromagnetic state of a medium is described by four vector fields, the electric and magnetic field vectors \mathbf{E} and \mathbf{B} , and the electric and magnetic displacement fields, \mathbf{D} and \mathbf{H} , which are all functions of the space and time coordinates, \mathbf{r} . The space and time derivatives of these fields are related to each other and to the macroscopic charge and current densities, ρ_e and \mathbf{j} by the *Maxwell equations* which are suppose to hold at each point in space and time where the derivatives of the field exist. They read as:

$$\begin{aligned} \nabla \wedge \mathbf{E} + \dot{\mathbf{B}} &= 0, & \nabla \cdot \mathbf{B} &= 0 \\ \nabla \wedge \mathbf{H} - \dot{\mathbf{D}} &= \mathbf{j}, & \nabla \cdot \mathbf{D} &= \rho_e \end{aligned} \quad (1a, b)$$

The field vectors $\mathbf{B}, \mathbf{H}, \mathbf{D}$ and \mathbf{E} are related by the constitutive relations:

$$\mathbf{B} = \mu_0 \mu_r \mathbf{H}, \text{ and } \mathbf{D} = \epsilon_0 \epsilon_r \mathbf{E}. \quad (2)$$

The functions $\epsilon_{0,r}$ and $\mu_{0,r}$ denote the dielectrical- and magnetical (relative) permeabilities resp., and are tensors in general. The physical significance and the unambiguous definition of the fields $\mathbf{E}, \mathbf{B}, \mathbf{D}$, and \mathbf{H} on the macroscopic level are based, on the one hand that in vacuo the fields satisfy $\mathbf{D} = \epsilon_0 \mathbf{E}$ and $\mathbf{B} = \mu_0 \mathbf{H}$ and give the force on a unit test charge or current, and on the other hand on the fact that the polarisation and magnetisation \mathbf{P} and \mathbf{M} , *defined* by the equations:

$$\mathbf{D} = \epsilon_0 \mathbf{E} + \mathbf{P}, \quad \mathbf{B} = \mu_0 \mathbf{H} + \mathbf{M} \quad (3)$$

are resp. the electric- and magnetic dipole moments per unit volume of the medium. These quantities should be derived from the underlying microscopical equations, and it was exactly this derivation which was initiated as early as 1878 by Lorentz [4] (for an English translation see [5, 6]). Further basic articles see: [7, 8]. Once it has become clear how the macroscopical Maxwell equations can be derived from

the microscopical Maxwell equations the relation between the polarisation, the magnetisation, and the microscopical structure of the medium is established. This then enables the analysis of the connection between refractive index and the microscopical material properties. It will be shown in particular that the Lorentz-Lorenz relation, also known as the Clausius-Mosotti equation, follows immediately by the transition from the microscopical- to the macroscopical equations. Moreover, the influence of statistical fluctuations of the density or on the refractive index will be calculated.

The outline of this paper is as follows: We start with the microscopical Maxwell equations and will then derive the corresponding macroscopical equations, viz. (1a, b) by the appropriate ensemble averaging procedures. The underlying physical assumptions will be discussed at length, as they essentially determine the final expression for the refractive index in terms of the microscopical properties of the medium.

The Calculation of the Polarisation

In this section we will derive the macroscopical Maxwell equations (1a, b) from the microscopical Maxwell equations:

$$\begin{aligned} \nabla \wedge \mathbf{e} + \dot{\mathbf{b}} &= 0, \quad \nabla \wedge \mathbf{b} - \dot{\mathbf{e}} = \mathbf{j} = \sum_{i,k} e_{k,i} \mathbf{R}_{k,i} \delta(\mathbf{R}_{k,i} - \mathbf{R}) \\ \nabla \cdot \mathbf{b} &= 0, \quad \nabla \cdot \mathbf{e} = \rho_e = \sum_{i,k} e_{k,i} \delta(\mathbf{R}_{k,i} - \mathbf{R}) \end{aligned} \quad (4a, b)$$

where ρ_e and \mathbf{j} denote the microscopic source and current distributions. Next we derive the the so-called atomic field equations, i.e. The Maxwell equations in which the existence of atoms (stable groups of point particles) has been taken into account. The position vector $\mathbf{R}_{k,i}$ of a stable group k of particles is written as:

$$\mathbf{R}_{k,i} = \mathbf{R}_k + \mathbf{r}_{k,i}, \quad (5)$$

where the $\mathbf{r}_{k,i}$ denote the internal coordinates, which specify the positions of the constituent particles k, i with respect to the position \mathbf{R}_k of the privileged group. Then, introducing the multipole expansions of the group of point charges:

$$\rho_e = \nabla \cdot \sum_{k,i} e_{k,i} \sum_{n=1}^{\infty} \frac{(-1)^{n-1}}{n!} (\mathbf{r}_{k,i} \cdot \nabla)^n \delta(\mathbf{R}_k - \mathbf{R}) \quad (6)$$

and

$$\mathbf{j} = \sum_{k,i} e_{k,i} (\dot{\mathbf{R}}_k + \dot{\mathbf{r}}_{k,i}) \sum_{n=0}^{\infty} \frac{(-1)^{n-1}}{n!} (\mathbf{r}_{k,i} \cdot \nabla)^n \delta(\mathbf{R}_k - \mathbf{R}) \quad (7)$$

and

$$\rho_e^{mono} = \sum_{k,i} e_{k,i} \delta(\mathbf{R}_k - \mathbf{R}) \quad (8)$$

we obtain:

$$\begin{aligned} \nabla \cdot \mathbf{e} &= \rho_e^{mono} - \nabla \cdot \mathbf{p}, & \nabla \wedge \mathbf{h} - \dot{\mathbf{e}} &= \mathbf{j} + \dot{\mathbf{p}} + \nabla \wedge \mathbf{m} \\ \nabla \cdot \mathbf{b} &= 0, & \nabla \wedge \mathbf{e} &= -\dot{\mathbf{b}} \end{aligned} \quad (9)$$

with

$$\mathbf{m} = \sum_k \mathbf{p}_k \nabla \dot{\mathbf{R}}_k + \sum_i e_{k,i} \sum_{n=1}^{\infty} \frac{(-1)^n n}{(n+1)!} \mathbf{r}_{k,i} \wedge \dot{\mathbf{r}}_{k,i} (\mathbf{r}_{k,i} \cdot \nabla)^{n-1} \delta(\mathbf{R}_k - \mathbf{R}) \quad (10)$$

and

$$\mathbf{p} = \sum_k \mathbf{p}_k; \quad \mathbf{p}_k = \sum_i e_{k,i} \sum_{n=1}^{\infty} \frac{(-1)^{n-1}}{n!} \mathbf{r}_{k,i} (\mathbf{r}_{k,i} \cdot \nabla)^n \delta(\mathbf{R}_k - \mathbf{R}). \quad (11)$$

The model we take for the medium is that we suppose that the medium consists of a randomly oriented collection of scatterers each of which experiences the field radiated by the excited other scatterers. For a macroscopic description to be valid the system has to satisfy certain general conditions. One of these is that it must be possible to divide the system into “physically infinitesimal” volume elements, of diameter Δ , which on one hand are small compared with distances over which the macroscopical variables vary appreciably, and which, on the other hand, contain so many molecules that the principles of statistical mechanics are applicable, and quantities like the entropy and the temperature can be defined for each volume element. We characterise these conditions by the basic inequalities:

$$a \ll \Delta \ll \lambda, \quad (12)$$

where a is a molecular dimension and λ is a length characterising the spatial variations of the macroscopic variables in the system. *This approximation is known as the local field approximation and constitutes the key assumption of all the theories of molecular optics!* It is then assumed that these scatterers are so widely separated that the various fields they experience from the other scatters are *dipole* fields. This assumption, usually justified in practice, simplifies the calculations enormously. However, once the calculations have been set up using this approximation, higher order multipole fields like quadripole-octipole etc. can be dealt with similarly [9]. The local field approximation and the dipole field approximation are exemplified in Fig. 1. The dipole at some place inside the medium experiences the field due to the contributions of all the dipoles outside a sphere, the so-called Lorentz sphere. These dipoles lead then to a depolarising field of magnitude $1/3\epsilon_0 \mathbf{P}(\mathbf{r})$ which makes that the dipole inside the sphere experiences a *local* field

$$\mathbf{P} = \rho a (\mathbf{E} + \frac{1}{3\epsilon_0} \mathbf{P}), \quad (13)$$

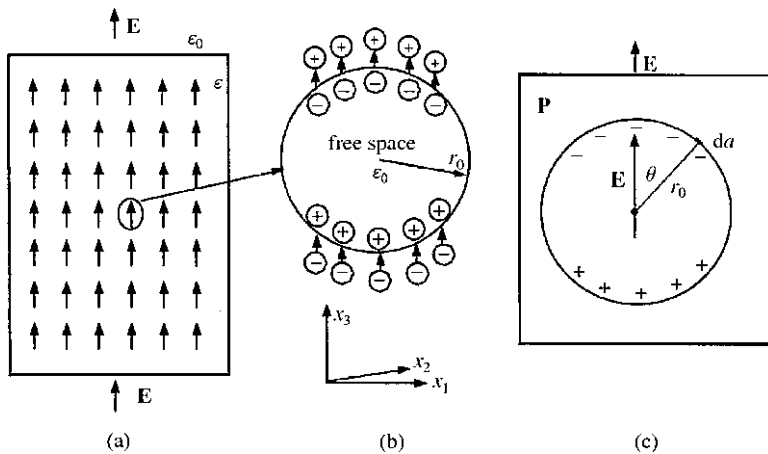


Fig. 1 (a) Macroscopical medium, (b) The Lorentz sphere, (c) The Lorentz sphere inside the medium.

If the dielectric were simple it would also be true that, see (2) and (3):

$$\mathbf{P} = (\epsilon_0 \epsilon_r - 1) \mathbf{E} \quad (14)$$

where ϵ_r denotes the relative dielectrical permeability. Combination of (13) and (14) then yields the Clausius-Mosotti or Lorentz-Lorenz law:

$$\epsilon_0 \frac{\epsilon_r - 1}{\epsilon_r + 2} = \frac{1}{3} \rho a, \quad (15)$$

where ρ denote the density of the dipoles with “dipole strength” a . We would like to stress the point that the choice of the particular form of the excluding geometry, viz. the Lorentz *sphere*, determines the numerical factor of the depolarizing field: $\frac{1}{3}$ for this case. If we had chosen a different geometry, another numerical factor would have occurred! This observation may well be of interest if we consider non-spherically symmetrical molecules, in which case another type of cavity e.g. an ellipsoidal one has to be chosen.

Now consider again a collection of dipoles, where each dipole is characterised by its polarisability tensor \mathbf{a}_i and give rise to a dipole with strength \mathbf{p}_i , if subject to an electric field $\mathbf{E}_0(\mathbf{r}_i)$

$$\mathbf{p}_i = \mathbf{a}_i \cdot \mathbf{E}_0(\mathbf{r}_i) \quad (16)$$

The polarisability tensor \mathbf{a}_i is the basic molecular quantity to be derived either classically or quantum mechanically from the structure of the constituents of the material under consideration. For a detailed derivation see [10].

Next, a dipole with dipole moment \mathbf{p}_i generates a field distribution:

$$\mathbf{p}_i \cdot \mathbf{F}_{i,j}, \quad (17)$$

with

$$\mathbf{F}_{i,j}(\mathbf{r}_i, \mathbf{r}_j) = (\nabla_i \nabla_i + k^2) \frac{\exp(-ikr_{i,j})}{r_{i,j}}, \quad (18)$$

where $r_{i,j}$ denotes the distance between the coordinates \mathbf{r}_i and \mathbf{r}_j , and the symbol ∇_i denotes the unit tensor of order and rank 3. The theory, and in fact *any* theory enabling the transition of microscopical- to macroscopical Maxwell equations is then based on the following integral equation:

$$\mathbf{p}_i = \mathbf{a}_i \cdot \left[\mathbf{E}_0(\mathbf{r}_i) - \sum_{j=1, j \neq i}^N \mathbf{F}_{i,j}(\mathbf{r}_i, \mathbf{r}_j) \cdot \mathbf{p}_j \right]. \quad (19)$$

The average dipole moment $\bar{\mathbf{p}}_i$, the average polarisability $\bar{\mathbf{a}}_i$, and the polarisation $\mathbf{P}(\mathbf{r})$ are given by:

$$\bar{\mathbf{p}}_i = \frac{\overline{\mathbf{p}_i \delta(\mathbf{r}_i - \mathbf{r})}}{\overline{\delta(\mathbf{r}_i - \mathbf{r})}} \quad (20)$$

and

$$\bar{\mathbf{a}}_i = \bar{\mathbf{a}} = \rho^{-1} \sum_i \overline{\mathbf{a}_i \delta(\mathbf{r}_i - \mathbf{r})} \quad (21)$$

and

$$\mathbf{P}(\mathbf{r}) = \sum_i \overline{\mathbf{p}_i \delta(\mathbf{r}_i - \mathbf{r})} = \sum_i \bar{\mathbf{p}}_i \overline{\delta(\mathbf{r}_i - \mathbf{r})} = \rho \bar{\mathbf{p}}_i \quad (22)$$

respectively, and the quantity ρ denotes the molecular density:

$$\rho = \sum_i^N \overline{\delta(\mathbf{r}_i - \mathbf{r})}. \quad (23)$$

Then, combination of equations (19)–(23) yields:

$$\mathbf{P}(\mathbf{r}) = \rho \bar{\mathbf{a}} \left[\mathbf{E}_0(\mathbf{r}) - \int_v \mathbf{F}(\mathbf{r}, \mathbf{r}') \mathbf{P}(\mathbf{r}') g^{(2)}(\mathbf{r}, \mathbf{r}') d\mathbf{r}' \right] + \mathbf{J}(\mathbf{r}), \quad (24)$$

if

$$\mathbf{J}(\mathbf{r}) = \int_V \sum_{i,j,i \neq j} \overline{[\bar{\mathbf{a}} \cdot \mathbf{F}_{i,j} \cdot \bar{\mathbf{p}}_j - \mathbf{a}_i \cdot \mathbf{F}_{i,j} \cdot \mathbf{p}_j]} \delta(\mathbf{r}_i - \mathbf{r}) \delta(\mathbf{r}_j - \mathbf{r}') d\mathbf{r}' \quad (25)$$

and $g^{(2)}(\mathbf{r}, \mathbf{r}')$ denotes the so-called pair correlation function

$$g^{(2)}(\mathbf{r}, \mathbf{r}') = \overline{\sum_{i,j,i \neq j} \delta(\mathbf{r}_i - \mathbf{r}) \delta(\mathbf{r}_j - \mathbf{r}')} \quad (26)$$

The first of these equations, (24) describes the dominant interaction, whereas the second one, (25) describes the deviations from the main process because its integrand denotes the difference between the mean (macroscopical) and the microscopical quantities. These equations are the basic equations of molecular optics and lead to the classical laws connected with the refractive index such as the Clausius-Mosotti (Lorentz-Lorenz) law see

$$(15): \rho^{-1} \frac{n^2 - 1}{n^2 + 2} = \frac{1}{3} \mathbf{a}_0(\omega)$$

A straightforward but tedious calculation [11] then leads to:

$$\rho^{-1} \frac{n^2 - 1}{n^2 + 2} = \frac{1}{3} \mathbf{a}_0 \frac{[1 + G(\rho, T, \omega)]}{1 + \rho \mathbf{a}_0(\omega) D} \left[1 + \frac{\Delta \bar{\mathbf{a}}}{\mathbf{a}_0(\omega)} + G(\rho, T, \omega) \right] \quad (27)$$

if

$$G(\rho, T, \omega) = \frac{\bar{\mathbf{a}}}{\mathbf{a}_0(\omega)} R, \quad \Delta \bar{\mathbf{a}} = \bar{\mathbf{a}} - \mathbf{a}_0(\omega). \quad (28)$$

The relation (27) has been for the first time derived by [12], see also [13, 14]. The functions $D(\rho, T, \omega)$ and $R(\rho, T, \omega)$ are defined by:

$$D(\rho, T, \omega) = \int_{V(\mathbf{r})}^V \mathbf{u} \cdot \mathbf{F}(\mathbf{r}, \mathbf{r}') \cdot \mathbf{u} \exp(-i n \mathbf{k} \cdot (\mathbf{r}' - \mathbf{r})) [g^2(\mathbf{r}, \mathbf{r}') - 1] d\mathbf{r}', \quad (29)$$

$$R(\rho, T, \omega) = \int_{V(\mathbf{r})}^V \mathbf{u} \cdot \mathbf{K}(\mathbf{r}, \mathbf{r}') \cdot \mathbf{u} \exp(-i n \mathbf{k} \cdot (\mathbf{r}' - \mathbf{r})) \quad (30)$$

resp. The wave vector \mathbf{k} is equal to $\frac{\omega}{c} \times$ the unit vector in the propagation direction. The vector \mathbf{u} denotes the unit vector in the direction of $\mathbf{P}(\mathbf{r})$. The basic result (27) contains the complete physical information of our system!! The fluctuations of the medium are described in terms of the average polarisability $\bar{\mathbf{a}}$ and the polarizability \mathbf{a}_0 of the free molecule. The tensor function $\mathbf{K}(\mathbf{r}, \mathbf{r}')$ is determined by the basic equations (24) and (25) and describes the fluctuations of the medium due to whatever course, such as density- temperature fluctuations.

The assumptions on which this refined model for the calculation of the refractive index equations is based together with the result (27) and the remarks made below

(15) constitute the basic tools for an in depth analysis of the results obtained by Albert Amat i Genís [1, 2, 3], showing an increasing refractive index proportional to the illumination time for a solution of ATP in water.

Discussion

In the previous sections we developed the theory of the refractive index and carefully stated various assumptions involved. These pertinent assumptions involved are listed below, together with a short statement concerning the implications for the values of the refractive index:

- (a) A Lorentz ellipsoid could replace the sphere, then the depolarisation field takes a different value: its magnitude becomes $\beta\epsilon_0\mathbf{P}(\mathbf{r})$ instead of $1/3\epsilon_0\mathbf{P}(\mathbf{r})$, where β can be any number between zero and one. The Lorentz-Lorenz relation (15) then changes because the local field equation (13) then becomes:

$$\mathbf{P} = \rho a(\mathbf{E} + \beta\epsilon_0\mathbf{P}), \quad (31)$$

- (b) The polarizability a is in general a tensor. This is probably true for the case considered by Albert. Amat and accounts for asymmetry effects.
- (c) Should only dipole-dipole interactions be considered or are quadripole- and octupole- etc. interactions important as well? These interactions become important if the interaction between the various dipoles is such that not only nearest neighbors interactions are important but also further neighbors interactions become important.
- (d) Are non-linear effects important? These effects become important if the field strength is sufficiently large.
- (e) The effect of the polarity of water was not considered. The large permanent dipole moment of water influences the value of the refractive index and may well account partly for the Amat effect as a changing geometrical shape of the ATP molecule leads to another distribution of the water molecules surrounding the molecule. An effective theory for such solutions is given by Onsager [15] and Böttcher [16–18].

These issues listed above may be of great value for the analysis and further understanding of the Amat effect.

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